ALUMINUM NITRIDE. PREPARATION METHODS[1]

A. A. Elagin,[2] A. R. Beketov,[2] M. V. Baranov,[2] and R. A. Shishkin[2]

Translated from *Novye Ogneupory*, No. 1, pp. 49 – 55, January, 2013.

Original article submitted September 4, 2012.

Russian and overseas sources published in the last twenty years for aluminum nitride preparation methods are studied. Both basic and relatively simple technology, as well as atypical innovative procedures, are analyzed, making it possible to form a complete picture of aluminum nitride preparation methods within the world.

Keywords: aluminum nitride, carbo- and methane-thermal reduction, nitriding, AlN single crystals, AlN films, AlN powder, laser ablation method, SHS method, combustion in alundum containers.

GAS PHASE REACTION OF LOW-VOLATILITY INORGANIC ALUMINUM COMPOUNDS WITH NITROGEN OR NITROGEN-CONTAINING COMPOUNDS

AlN powder, activated with rare-earth metals (RE), and its preparation method according to a patent in [44] was developed for manufacturing and improving nitride semiconductors, activated with RE ions. The additions to aluminum used were Dy, Tb, Eu, Tm, Ho, Sm, Er, Nd, Pr, Gd and combinations of them. It is desirable to use additions selected from Tb, Eu, Tm, Dy, and combinations of them, as a result of the best photoluminescence properties. The preferred preparation method includes several stages. At first aluminum nitrate, as also the RE, are dissolved in deionized water. The required amount of ammonium hydroxide is added in order to form a semihard gel of combined aluminum and RE hydroxides, which is filtered. Then hydroxides are washed with deionized water to a constant pH value:

$$xRE(NO_3)_3\,l + (1-x)Al(NO_3)_3\,l + 3NH_4OH\,l = Al_{1-x}RE_x(OH)_3\,so + 3NH_4NO_3\,l. \quad (10)$$

In the second stage cleaned hydroxide reacts with concentrated ammonium fluoride at 80°C in accordance with the following reaction:

$$Al_{1-x}RE_x(OH)_3\,so + 6NH_4F\,l = (NH_4)_3Al_{1-x}RE_xF_6\,so + 3H_2O\,l + 3NH_3\,g. \quad (11)$$

In the third stage fluoride product of the second stage is placed in a furnace and dried for 12 h at 200°C. Once-dried $Al_{1-x}RE_x(OH)_3$ is heated in an ultrapure ammonia atmosphere at high temperature (desirably ~900°C for 2.5 h) for complete conversion of fluorides into nitrides:

$$(NH_4)_3Al_xRE_{1-x}F_6\,so + NH_3\,g = Al_xRE_{1-x}N\,so + 6NH_4F\,g. \quad (12)$$

The final product is a compound $Al_xRe_{1-x}N$ containing alloying additions, controlled by addition of different first stage nitrates. It has been detected that the final product of the second stage may contain tetrafluorides $Al_xRE_{1-x}N$. in addition to hexafluorides $(NH_4)3Al_{1-x}RE_xF_4$. Although the ammonium aluminohexafluorides dissolve well in water at room temperature, in contrast to Ga and In, a white residue always remains after the second stage. The elemental analysis of this residues shows presence of oxygen, which is quite complicated to remove in the course of ammonia treatment. In order to obtain highly pure aluminum nitride is it necessary to remove the oxygen source at the end of the second stage. This was achieved by an increase in liquid ammonium fluoride quality, taken in excess from a stoichiometric ratio, and acceleration of reaction due to an increase in temperature. Subsequent elemental analysis of AlN at the end of the third stage showed a lower oxygen content and absence of any second phase in final product.

Rapid solid-phase reactions for AlN preparation are described in [45]. The following starting substance were taken: $AlCl_3$ (99.99%), Al_2S_3 (99.9%), Li_3N (99.5%), and Ca_3N_2 (99%). Aluminum iodide (AlI_3) was prepared by heating elements that comprise it (Al 99.5% and I_2), and taken from a tube in the gas phase due to a temperature gradient from 463

[1] Conclusion. For beginning see No. 11 for 2012.

[2] FGAOU VPO Ural Federal University, Ekaterinburg, Russia.

to 623 K (as for generally known GaI_3 preparation). The AlN obtained was transferred to a chamber for operation with hazardous materials, filled with helium. The amount of AlN obtained was 0.20 g (4.8 mole). Reagents were taken in a stoichiometric ratio, mixed and ground in a mortar, stirred in a stainless steel or ceramic crucible, and then in a larger open reaction vessel. This made it possible to retain gases liberated in the course of reaction. The reaction was initiated on heating by means of a nickel-chromium heater, made in the form of a wire. The solid-phase reaction was exothermic, as a result of which the reaction may commence spontaneously on mixing reagents. Reaction products are then removed from a drying chamber, and washed in 0.1 M HCl or 1.0 M H_3PO_4. During removal of subsidiary salts by washing with water, acid provides self-catalytic hydrolysis of the product. In order to reduce the duration of AlN in aqueous solution the product is slowly filtered in a vacuum through a glass microfiber filter paper and dried in a furnace at 450°C. Solid phase reactions may be described by the following equations:

$$AlCl_3 + Li_3N = AlN + 3LiCl,\ T = 1513\ K, \quad (13)$$

$$0.5Al_2S_3 + Li_3N = AlN + 1.5Li_2S,\ T = 1373\ K, \quad (14)$$

$$AlCl_3 + 0.5Ca_3N_2 = AlN + 1.5CaCl_2,\ T = 1673\ K. \quad (15)$$

In choosing aluminum-containing and nitrogen-containing reagents consideration should be given to stability of the products with respect to reagents, temperature, with which there are reagent phase transformations, and the maximum reaction temperature. Consequently, products should be more stable than reagents in order to provide spontaneous exothermic reaction. Addition of such nitrogen-containing reagents as NH_4Cl, NaN_3, and $LiNH_2$ to an original mixture (as also addition of AlN as a primer) only leads to an increase in content of impurities in final product. Reaction at lower temperature leads to an increase in impurity content, and in fact aluminum oxide in final product. Therefore, the highest temperature exothermic reaction should be selected, i.e., reaction of ammonium chloride with calcium nitride, proceeding at above 2100 K. This method makes it possible to achieve pure AlN preparation rapidly.

According to data in [46] it is also possible to obtain AlN by combustion in a gas phase

$$AlCl_3 + NH_3 + 50Ar = AlN + 3HCl. \quad (16)$$

The yield from reaction (16) is very modest, i.e., less than 30% with NH_3 stoichiometry, but yield increases with an increase in NH_3 or N_2 content, and an excess of the stoichiometric ratio by a factor of 50 gives a yield close to 100%. The main reason for a low yield with a stoichiometric ratio is NH_3 decomposition. Examples have been obtained thermodynamically close to the ideal. It is possible to reduce the probability of ammonia breakdown with correct choice of reactor materials and formation of stable products $AlCl_3 \cdot (NH_3)_n$ ($n = 1 – 6$). In fulfilling these conditions yield increases to 70% with a six-fold excess of NH_3 at 1000°C. An inherent limitation of reaction (16) is the fact that in order to obtain the optimum reaction rates there should be a high temperature, although is provokes NH_3 decomposition, and this reduces yield. It should also be considered that the products obtained as a result of hydrolysis only contain 3 wt.% oxygen. Addition of sodium to the $AlCl_3$–NH_3 system may strongly increase the thermodynamic yield with decomposition of NH_3 or without it. As a result of this a yield close to 100% is obtained in this system over a wide temperature range. In addition, reaction with addition of sodium has a number of advantages with respect to reaction (16). First, the reaction is exothermic (2 – 1244 kJ/mole), as a result of which there is a reduction in energy consumption. Second, the subsidiary gas product is hydrogen, which may be used as a result of its high thermal value, compared with HCl, which should be collected.

A gas-phase method for preparing AlN powder from $AlCl_3$–NH_3–N_2 is described in [47]. The source of aluminum was selected as aluminum chloride of 98% purity. The sublimation temperature for ammonium chloride is 177.8°C. It was placed in a glass tube and heated to 180°C in an oil bath. Nitrogen was passed through the glass tube in order to remove moisture and oxygen. Aluminum chloride vapor, mixed with high purity nitrogen 99.99% was fed to the central area of the furnace. A strip heater was used in order to prevent aluminum chloride condensation. Then pure ammonia (99.999%) was added to the heated zone. The reactor is a quartz tube, located within a furnace. At the reactor outlet there was a round flask for recovery of powder emerging from the reactor, and in order to extinguish any pressure variations outside the reactor. Synthesis lasted 1 h. The rate of AlN yield was 0.15 – 5.5 g/h:

$$AlCl_3\ g + NH_3\ g = AlN\ so + 3HCl\ g \text{ at above } 700°C, \quad (17)$$

$$AlCl_3\ g + 4NH_3\ g = AlN\ so + 3NH_4Cl\ so \text{ at about } 350°C. \quad (18)$$

Below 250°C ammonium chloride may be obtained

$$NH_3\ g + HCl\ g = NH_4Cl\ so. \quad (19)$$

It is seen from reactions (17) – (19) that AlN and HCl may be obtained within a reactor, if the reaction temperature is quite high in order to suppress reaction (18). At the same time, it is possible to obtain AlN and NH_4Cl by reactions (18) and (19) from unreacted $AlCl_3$, NH_3, and HCl. This is possible on condition that the temperature outside flask is quite low. Above 130°C there is ammonia dissociation:

$$2NH_3 = N_2 + 3H_2. \quad (20)$$

In turn nitrogen is not so capable of reaction and reluctantly reacts with ammonium chloride. The maximum yield

may be obtained with suppression of ammonia dissociation. With a molar ratio of NH_3:AlC_3 = 1.5 in the range from 700 to 1000°C a very low yield is obtained, 20% in total. With an increase in molar ration the yield increases. With a molar ratio of 6:1 at 1000°C the yield may reach 70%, and with a ratio of 8:1 it reaches 80%. As a result of this reaction spheroidal shaped powder is obtained with particle sizes of 0.1 – 1.0 μm.

A method of synthesizing single-crystal AlN, described in a patent [48], is based on reaction of gaseous ammonia compounds and nitriding reagent or in the presence of active metal in the high-temperature zone. Crystals of AlN obtained are deposited on a condenser. The process may be represented by the following reactions:

$$3AlCl\ g + N_2\ g = 2AlN\ so + AlCl_3\ so, \quad (21)$$

$$2Al + MgF_2 = 2AlF + Mg, \quad (22)$$

$$2AlF\ g + Mg\ g + N_2\ g = 2AlN\ so + MgF_2\ so. \quad (23)$$

The degree of aluminum oxidation in compounds should be less than +3, i.e., this is such compounds as AlBr, $AlCl_2$, AlF_2, AlOH, AlI, Al_2S, AlO, AlS, Al_2O, or mixtures of them. It is preferred to use aluminum monochloride or monofluoride, or a mixture of them. The nitriding agent used may be any compound, within whose composition there are nitrogen atoms or molecules which under certain conditions may be liberated. Reaction is carried out at a pressure of the order of 1 atm. in presence of inert gas (for example argon). Crystals with a size of 1 – 15 μm are obtained as a result of reaction

According to technology described, developed by scientific colleagues of the faculty of rare metals and nanomaterials of the Ural Federal University Physicotechnical Institute [49 – 52], methods have been developed for preparing high purity AlN in different forms by reaction of gaseous ammonium trifluoride with molten aluminum with formation of aluminum monofluoride, and then its reaction with nitrogen-containing gas. The preparation method is described by two main reactions:

$$2Al\,l + AlF_3\ g = 3AlF\ g, \quad (24)$$

$$3AlF\ g + N_2\ g = 2AlN\ so + AlF_3\ g. \quad (25)$$

Preparation of aluminum monofluoride is carried out in a rotary furnace at 1000 – 1300°C by loading a charge of solid aluminum and ammonium trifluoride, and reaction with nitrogen-containing gas is carried out at the surface if a charge, and gas is fed counter to charge movement [53]. The reaction is accomplished at atmospheric pressure. The method provides preparation of very fine highly pure AlN powder, suitable for use in electronics and electrical engineering, and also for creating heat-conducting ceramic objects for use as insulators and as heating unit lining elements.

REACTION OF INORGANIC ALUMINUM COMPOUNDS WITH NITROGEN-CONTAINING ORGANIC COMPOUNDS OR NITROGEN

The method of AlN formation through an organic precursor from anhydrous aluminum chloride and diethyldiamine has been described in an article [54]. In this method anhydrous $AlCl_3$ and diethylamaine $H_2NCH_2CH_2NH_2$ (DA) are used as sources of aluminum and nitrogen without further purification. Liquid DA is placed in a flask in order to create a dry nitrogen atmosphere (99.99%). Anhydrous $AlCl_3$ is slowly added to liquid DA to a molar ratio of 1:10 at room temperature; simultaneously there is flushing with dry nitrogen. The suspension obtained is evaporated with an increase in temperature, then a brownish-white solid product is rapidly precipitated. The solid product is dried at 150°C for 2 h in a dry nitrogen stream in order to remove DA residues, after which it is treated in a vacuum at 100°C for 3 h. The powder may be prepared with calcining for 5 h at 800 – 1200°C in a tubular electric furnace with flushing of dry nitrogen. A carbon fiber, placed in the upper part of the tube, is used in order to exclude access of oxygen during flushing of the calcined powder with dry nitrogen. The particle size obtained by this method is less than 25 nm, but due to agglomeration it varies in the range 60 – 400 μm.

In order to obtain AlN by nitriding oxygen-containing aluminum compounds [55] $Al(NO_3)_3{\cdot}6H_2O$ (99.999%), 2-ethylhexanoate (96%) and $Al(OH)_3$ in the form of a gel (>98%), which was previously dried at 180°C for 2 h, at 100°C for 2 h, and 100°C for two days respectively are used, and $Al(OCH\mathit{Me}_2)_3$ was evaporated during hydrolysis in an NH_3 atmosphere, $(Al(N\mathit{Me}_2)_3)_2$ was prepared from $AlCl_3$ and $LiN\mathit{Me}_3$, $AlH_3{\cdot}N\mathit{Me}_3$ from $LiAlH_4$ and $\mathit{Me}_3N{\cdot}HCl$. Before hydrolysis reagents were ground in a mortar. All of the operations were carried out in a dry nitrogen atmosphere in a cabinet for operating with hazardous substances. A furnace was made in the form of a tube with a corundum lining. The vessel for charging the starting reagents was an alundum boat, and previously the tube and boat were heated to 1500°C and nitrided in an atmosphere of dry ammonia. The reagents were used in small amounts. The rate of gas flow was 85 and 10 cm^3/min for pyrolysis in ammonia and 50 cm^3/min for pyrolysis in nitrogen. Gas purity was 99.9995% for both pure ammonia and nitrogen. The heating rate was 3° C/min, holding for 2 h. Then specimens were heated to 1000 – 1400°C.

With pyrolysis of ammonium nitrate particles of the AlN obtained had a size of 10 – 50 μm, with pyrolysis of hydroxide they were 5 – 25 μm, but with use of organic compounds they were less than 500 μm. AlN powder, obtained at 1400°C from hydroxide and nitrate, contained 2.5 and 2.25 wt.% oxygen respectively. AlN powder, obtained at 1500°C from hydroxide, contained 1.50 wt.% oxygen, and powder prepared at 1500°C from organics contained 0.83 wt.% oxygen. Compounds $Al(N\mathit{Me}_2)_3$ and $AlH_3{\cdot}N\mathit{Me}_3$ are normally considered suitable as reagents for AlN preparation, but in the course of

these tests in a nitrogen atmosphere either a small amount of AlN was obtained, or none at all.

REACTION OF ORGANIC COMPOUNDS CONTAINING ALUMINUM AND NITROGEN-CONTAINING ORGANIC COMPOUNDS OR NITROGEN

According to data in [56] preparation of highly pure AlN is achieved due to reaction of aluminum vapor with organic compounds, such as triethyl aluminum, in a stream of ammonia. A heated gaseous aluminum-containing organic compound is fed to the reaction zone; ammonia also enters the reaction zone. Thus, a heated mixture (500 – 800°C) of aluminum-containing organic compound and ammonia reacts with formation of highly pure AlN powder. Aluminum nitride is deposited on a substrate, made of any suitable material, for example high-purity graphite, coated with pyrographite. As a result of this highly pure AlN is obtained with an impurity (0.00005 wt.%) silicone.

The method for preparing AlN by carbothermal reduction and nitriding with use of aluminum dicarboxychelates is described in [57]. Preparation of AlN is accomplished from the aluminum compound $Al(OH)(C_{n+2}H_{2n}O_4)\cdot xH_2O$, where $n = 3, 6, 8$. In order to prepare AlN it is not necessary to mix this compound with any additions. Both crystalline and amorphous reagents were prepared for synthesis and dried at 40°C. Then aluminum dicarbochelate was calcined in a stream of nitrogen (200 ml/min) by two different methods: 1) the powder was calcined in a graphite crucible placed in a reactor made in the form of a tube of aluminum oxide and previously heated to the calcining temperature; 2) powder was placed in an alundum crucible, then at room temperature in a reactor made in the form of an aluminum oxide tube, and then heated to the calcining temperature. The heating rate was 5°C/min. Nitrogen, used for the carbothermal nitriding reaction, was purified from oxygen with passage through a tube containing carbon at 900°C. The remaining carbon was burnt off in the course of subsequent heating at 700°C in an air atmosphere for 1 h. Specimens were dehydrated with calcining at 400°C; dehydration was characterized by weight loss, which steadily decreased up to 600°C. Calcining of specimens was performed in the range 1100 – 1400°C for 2 h in a stream of nitrogen. With an increase in calcining temperature the density of AlN powder increased, although there was agglomeration into particles with a diameter of 0.2 μm. Thus, acicular AlN particles were obtained, and this gives to significant property anisotropy.

Preparation of AlN by means of carbothermal reduction in the presence of a burnt precursor is described in [58]. The starting reagents used were $Al(NO_3)_3\cdot 9H_2O$ (99%), $(CO(NH_2)_2$ (99%) and $C_6H_{12}O_6\cdot H_2O$. First a solution was prepared by dissolving reagents (aluminum nitrate, urea, and glucose) in water. Then the solution was heated in an electric furnace to 90 – 100°C. As a result of solution evaporation a gel-like mass was obtained. On holding the solution suddenly started to boil, and increased in volume, since a considerable amount of gas was released. The whole process took several minutes, as a result of which a black foamy mixture of aluminum oxide and carbon ($Al_2O_3 + C$) was obtained. The nitriding reaction was carried in a vertical graphite furnace. The mixture was placed in a graphite crucible. Before heating air was evacuated from furnace and filled with nitrogen in order to remove oxygen before the start of reaction. The mixture in a crucible was placed in the furnace, heated in a stream of nitrogen to 1000 – 1600°C for 120 min. The flow rate was 3 liter/min. The carbon remaining was burnt off from the final product in an air atmosphere at 700°C for 60 min. Completeness of the reaction was achieved with temperatures above 1400°C, and therefore it is desirable to carry out synthesis in the range 1400 – 1600°C. Ultrafine AlN powder is obtained as a result of this reaction.

A solidifying polymer precursor for AlN preparation is presented in data in [59]. Polymers, containing AlN, prepared with reaction of unsaturated organic nitrile with the formula *RCN*, where *R* is

2 – 12-carboalkene or alkene group, with dialkene aluminum hydrate with the formula $R'R''AlH$, where R' and R'' identical (or different) 1 – 12-carboalkene groups, up to the form of organoaluminum imine, which is heated from 50 to 400°C. Then polymer, containing AlN, may be dissolved in organic solvents not containing hydrogen ions (hexane, toluene, diethyl, etc.) and treated with ammonia or basic amine R^4NH_2, where R^4 is 1 – 12-carboalkene, cycloalkene, alkane, cycloalkane or aryl group for introducing HN- or R^4N-groups into polymer with reaction of transamination splitting off RCH_2NH_2 or splitting of aluminoalkene bonds.

Aluminum nitride is obtained as a result of pyrolysis at 800 – 2200°C, more desirably at 1200 – 2000°C, and the best conditions at 1400 – 1700°C. Pyrolysis in an ammonia atmosphere may be performed at below 600°C. By means of this method it is possible to obtain films, filaments, and coatings.

According to data in [60], AlN is obtained from alkaline ammonia salt. Ammonia alkyl is fed to a reactor in a gas phase and heated to 600 – 1400°C in an ammonia atmosphere, and a molar ratio from 1:1 to 1:100 respectively. As a result of this amorphous AlN powder is obtained which is calcined at 900 – 1200°C in a reducing atmosphere for 0.5 – 10 h. In order to remove carbon AlN is calcined at 1500 – 1700°C in an inert atmosphere for 2 – 5 h. The oxygen and carbon content in the powder obtained are 1.0 and 0.1% respectively.

Another interesting method for preparing AlN is provided in a patent [61]. Carboxyl aromatic acids are used, containing the group $–COOAl(OH)_2$, which is prepared with a solution of inorganic aluminum compounds and carboxyl aromatic acid in water, or in an aqueous solution of alkanes in the ratio 1:3 at 60 – 90°C. The compound is calcined at 1000°C for 1 h in an inert atmosphere (nitrogen or argon). With a low pH value inorganic substances have a tendency

towards low reaction yield, and therefore it is desirable to maintain pH in the range 4 – 6; with a higher pH the aromatic compound will not react entirely. Aluminum-containing salts of carboxyl aromatic compounds are insoluble in water, and therefore they may be readily separated in solution. After this the salt is heated in presence of nitrogen to obtain AlN. The heating temperature is 1400 – 1650°C, process duration 2 h. Then the remaining carbon should be burnt off in order to obtain pure AlN. Firing is performed at 600 – 700°C for 1 – 4 h in an oxidizing atmosphere. The spherical particles of AlN are prepared agglomerate into particles a diameter of 1 – 10 μm.

According to data published in a patent [62] it is possible to prepare AlN in a gas phase using organic aluminum compounds. Ammonia, heated to 300 – 600°C, is passed through a tube in a reactor. At the same time nitrogen-containing gas is fed to the reactor, containing organic aluminum compounds. Then heat treatment of AlN agglomerate obtained follows at 800 – 1100°C in a reducing atmosphere. As a result of this AlN powder is obtained with an average particle size of less than 0.06 mm, the degree of agglomeration is less than 10, and the impurity content in final product is less than 300 ppm.

COMBINED ALUMINUM NITRIDE PREPARATION METHODS

Preparation of filamentary AlN, according to data in [63], is possible by combining several methods for AlN preparation, and in fact:

1. SHS. Reaction of direct nitriding (exothermic reaction):

$$Al + N_2 = AlN_i + AlN_{sp}. \quad (26)$$

2. Reaction of carbothermal nitriding (endothermic):

$$Al_2O_3 + 3C_2 + N_2 = 2AlN_{(f+sp)} + 3CO\ g. \quad (27)$$

3. Gas-phase method:

$$Al/Al_2O_3 + HCl/Cl_2 = AlCl_3 = (N_2)AlN_f + AlN_{sp}. \quad (28)$$

In reactions (26) – (28) "f" signifies that AlN is a filamentary form of particles, and "sp" is spherical. Reaction (26) is exothermic. Heat is absorbed in a carbothermal method by reaction (27). The result of combining these two reactions is less supply of energy to the system from outside in order to maintain reaction. As a result of reaction a combination of AlN is obtained in the form of filaments and particles. It is necessary once to supply heat for initiating the SHS reaction, then the reaction itself will generate heat for occurrence of the rest of the process. In endothermic reaction (27) aluminum oxide in the from of powder reacts with carbon and nitrogen, as a result of which a mixture AlN filaments and particles, and carbon monoxide is obtained. The fact that reaction is endothermic, helps regulate and stabilize reaction temperature in the furnace. In well-known exothermic synthesis of filamentary AlN the reaction temperature should be controlled by means of external cooling attachments, such as circulating cooling gases or liquids. Here the carbothermal reaction does not develop high SHS reaction temperatures in a furnace. If the temperature is not held below the melting of aluminum oxide, then there is an increase in apparent density of the reacting layer (since porosity is reduced) and free nitrogen may react with aluminum oxide quite effectively for a high yield. In addition: if the reaction temperature exceeds 2000°C, the filaments formed may also be broken.

In addition to the first two reactions content of filaments depends on the mechanism of the third reaction. It is assumed that fluorine atoms and ions produced (chloride ions) are liberated from ammonium chloride, and as hydrogen chloride facilitate a transport reaction within which aluminum or aluminum oxide reacts with chlorine atoms and chloride-ions. Transport gases or halogenides react with reduced aluminum or aluminum-containing ions to aluminum chloride, which is transferred to the area of filament growth in a fluidized bed in a vessel. Aluminum oxide is reduced and reacts with nitrogen to AlN, almost entirely consisting of filaments. This mechanism has not yet been studied entirely. However, it is understood that the filament content increases from 20- to 60 vol.% with an average yield from 35 to 40 vol.% with simultaneous occurrence of all three reactions. With excess chlorine (or chloride-ions) the filament content also increases.

USE OF AlN

Due to its valuable physicochemical properties aluminum nitride is used extensively in high-temperature technology as a refractory and electrical insulating material [64]. Electrical insulation sheaths for thermocouples and electrically insulating structural components are prepared from it, operating in corrosive media. The high refractoriness of AlN and chemical stability make it possible to use it for lining electrolyzers, baths, tanks, crucibles for preparing molten aluminum, tin, gallium, molten glass, and boric anhydride at 1300 – 2000°C [65].

Aluminum nitride is used for creating composite materials. With addition of AlN to a polymer matrix there is an improvement in physicochemical and physicomechanical properties of composite material such as thermal conductivity, electrical resistance, wear resistance, etc. [66]. Aluminum nitride is used as an addition in preparing copper paints with high thermal conductivity or corrosion resistance [67]. Films of AlN are used in microelectronics in manufacturing micromodules [68], integrated circuits, and also as active elements [69 – 71]. Due to high corrosion resistance towards molten salt media AlN coatings are used in the nuclear industry [72].

Aluminum nitride is added (30 wt.%) to nickel or aluminum [73]; there is a reduction in LTEC, thermal stresses, and an increase in microhardness and density. Specimens only exhibit open porosity, and matrix grain size (in particular nickel) hardly increase on sintering.

Together with titanium nitride AlN is used for coating steel, operating in corrosive media, such as water vapor at 600°C, sodium chloride, etc. The best properties, and in fact adhesion and microhardness, have been obtained with use of modifications of $(Ti_{0.6}Al_{0.4})N$. In this ratio corrosion was not observed at above 800°C and holding for 10 h [74].

CONCLUSION

A study is presented in this article of Russian and overseas sources for AlN preparation methods. Sources included the most interesting monographs, scientific articles, and patents for inventions, industrial examples, and useful models. On the basis of analyzing the data provided both basic and relatively simple technology, and also non-standard innovative procedures have been selected and presented, making it possible to formulate a complete picture for AlN preparation methods in the world.

Classification of preparation methods with respect to basic mechanism of chemical reaction for starting components made it possible to separate five comprehensive groups and to combine methods with a mixed type of chemical reaction into six groups, which makes it possible to find rapidly a description of a required method or see the main production principles of a group of methods as a whole. However, a study of the data presented showed that AlN, prepared by means of different methods, even within the scope of one group of methods, may differ considerably with respect to physicomechanical properties, equipment formulation, and economic expenditure for accomplishing it. Therefore in selecting a preparation method it is mainly necessary to proceed from requirements that are laid down for a nitride material for producing objects in some particular branch. Today, mainly as critical AlN parameters thermal conductivity and resistance at elevated temperature with respect to solid or liquid metals are selected. Of the most assimilated technology today SHS with aluminum metal in a nitrogen atmosphere, or carbothermal reduction of aluminum oxide in a nitrogen atmosphere are used. Each of these methods has disadvantages with certain simplicity of the production formulation. In order to produce objects in new branches, materials are required with improved physicomechanical properties with simultaneously relatively low production expenditure for implementing preparation technology. This may explain the steady search for new and improved methods of preparing these materials, and this is reflected in this review.

The study was carried out with financial support of Young Scientists of URFU within the scope of implementing the URFU development program.

REFERENCES

44. H. Bing, Jonathan H. Tao, R. Madis, Keith A. Klinedinst, Jan B. Talbot, and Kailash A. Mishra, US Patent 7935325, Rare earth-activated aluminum nitride powders and method of making (2011).
45. R. A. Janes, M. A. Low, and R. B. Kaner, "Rapid solid-state metathesis routes to aluminum nitride," *Inorg. Chem*., **42**(8), 2714 – 2719 (2003).
46. R. L. Axelbaum, C. R. Lottes, J. I. Huertas, and L. J. Rosen, *Gas-phase combustion synthesis of aluminum nitride powder. Twenty-Sixth Symposium*; A. R. Burgess and F. L. Dryer (editors) Pittsburgh: Combustion Institute (1996).
47. J. R. Park, S. W. Rhee, and K. H. Lee, "Gas-phase synthesis of AlN powders from $AlCl_3$–NH_3–N_2," *J. Mat. Sci*., **28**(1), 57 – 64 (1993).
48. Gilbert S. Layne, US Patent 3598526. Method for preparing monocrystalline aluminum nitride (1971).
49. Yu. D. Afonin, A. R. Beketov, L. D. Proskuryakov, L. M. Zhukova, and V. P. Ryabov, RF Patent 2074109, Method for preparing aluminum nitride (1997).
50. Yu. D. Afonin, D. A. Beketov, and N. L. Chernyi, RF Patent 2312060, Method for preparing aluminum nitride (2007).
51. Yu. D. Afonin, A. R. Beketov, L. M. Zhukova, and A. A. Panyushkin, RF Patent 2106298, Method for preparing fibrous aluminum nitride (1998).
52. Yu. D. Afonin, A. R. Beketov, A. V. Anipko, V. B. Malkov, and A. N. Cherepanov, RF Patent 2312061, Method for preparing fibrous aluminum nitride (2007).
53. A. A. Elagin, A. R. Beketov, Yu. D. Afonin, D. A. Beketov, M. V. Baranov, and R. A. Shishkin, RF Patent 117153, Device for preparing high purity aluminum nitride powder (2012).
54. Masataka Kano, Takeo Hyodo, Yasuhiro Shimizu, and Makoto Egashira, "Formation mechanism of aluminum nitride powder via organic precursor prepared from anhydrous aluminum chloride and 185 – 190 (2002).ethylenediamine," NAOSITE : Nagasaki University's Academic Output SITE, 32(59),
55. E. Kroke, L. Loeffler, F. F. Lange, and R. Riedel," Aluminum nitride prepared by nitridation of aluminum oxide precursors," *J. Amer. Ceram. Soc*., **85**(12), 3117 – 3119 (2002).
56. Joseph J. Gebhardt, US Patent 5356608. Preparation of a high purity aluminum nitride antenna window by organometallic pyrolysis (1994).
57. W. S. Jung and S. K. Ahn Jung, "Synthesis of aluminum nitride by a modified carbothermal reduction and nitridation method using basic dicarboxylate Al(III) complexes $Al(OH)(Cn + 2H_2NO_4)\cdot x(H_2O)$ (n = 3, 6, 8)," *J. Europ. Ceram. Soc*., **21**(1), 79 – 85 (2001).
58. M. L. Qin, X. L. Du, Z. X. Li, I. S. Humail, and X. H. Qu, "Synthesis of aluminum nitride powder by carbothermal reduction of a combustion synthesis precursor," *Mat. Res. Bull*., **43**(11), 2954 – 2960 (2008).
59. James A Jensen, US Patent 5260397. Thermoset polymeric precursor for aluminum nitride (1993).
60. Wakimura, Kazuo, Tanaka, Masao, Hiai, and Atsuhiko, US Patent 5110575 US. Process for producing sinterable crystalline aluminum nitride powder (1992).
61. Kataoka, Ryohei and Taga, Genji, European Patent A1 0558842. Process for preparing aluminium nitride powder (1992).
62. Yamazaki Masato, Mitsuishi Takeyuki, Tanaka Masao, and Harada Isao, Japanese Patent. 2007 – 182340. Aluminum nitride powder, its production method (2007).
63. Vithal Revankar and Arvind Goel, US Patent 5693305 US. Method for synthesizing aluminum nitride whiskers (1997).

64. Alan W. Weimer, Gene A. Cochran, John P. Henley, and Glenn A. Eisman, US Patent 5219804. Process for preparing ultrafine aluminum nitride powder (1993).
65. J. T. Oh, P. Hing, H. S. Fong, et al., "The processing of cordierite glasses containing AlN," *J. Mat. Proc. Technol.*, **63**(1 – 3), 851 – 854 (1997).
66. Y. S. Xu, D. D. L. Chung, and C. Mroz, "Thermally conducting aluminum nitride polymer-matrix composites," Composites Part a-Applied Science and Manufacturing, **32**(12), 1749 – 1757 (2001).
67. Terry Bloom US Patent 6207288. Copper ink for aluminum nitride (2001).
68. A. F. Belyanin, L. L. Bouilov, V. V. Zhirnov, et al., "Application of aluminum nitride films for electronic devices," *Diamond and Related Materials*, **8**(2 – 5), 369 – 372 (1999).
69. C. K. Lee, S. Cochran, A. Abrar, et al., "Thick aluminium nitride films deposited by room-temperature sputtering for ultrasonic applications," *Ultrasonics*, **42**(1 – 9), 485 – 490 (2004).
70. M. Moreira, J. Bjurstrom, I. Katardjev, and V. Yantchev, "Aluminum scandium nitride thin-film bulk acoustic resonators for wide band applications," *Vacuum*, **86**(1), 23 – 26 (2011).
71. C. Cibert, M. Chatras, C. Champeaux, et al., "Pulsed laser deposition of aluminum nitride thin films for FBAR applications," *Appl. Surface Sci*., **253**(19), 8151 – 8154 (2007).
72. K. Natesan, C. B. Reed, D. L. Rink, and R. C. Haglund, "Development and performance of aluminum nitride insulating coatings for application in a lithium environment," *J. Nuclear Mat*., **258**, 488 – 494 (1998).
73. K. Atarashiya, "Aluminum nitride metal composites using ultra-fine aluminum particles and their application for joining," *J. Mat. Proc. Technol*., **54**(1 – 4), 54 – 59 (1995).
74. M. S. Li, F. H. Wang, Y. H. Shu Li, et al., "Composite coatings of titanium-aluminum nitride for steel against corrosion induced by solid NaCl deposit and water vapor at 600°C," *Mat. Res*., **7**(1), 27 – 33 (2004).